

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 February 2005 (17.02.2005)

PCT

(10) International Publication Number
WO 2005/013924 A1

(51) International Patent Classification⁷: A61K 6/10

(21) International Application Number:
PCT/EP2004/007928

(22) International Filing Date: 16 July 2004 (16.07.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
03016195.4 17 July 2003 (17.07.2003) EP

(71) Applicant (for all designated States except US): 3M ESPE AG [DE/DE]; ESPE Platz, 82229 Seefeld (DE).

(72) Inventors: and

(75) Inventors/Applicants (for US only): KLETTKE, Thomas [DE/DE]; Graf-Berchthold-Strasse 1a, 86911 Diessen (DE); FUEHRER, Cornelia [DE/DE]; Schimmelreiterweg 4, 87497 Wertach (DE).

(74) Common Representative: 3M ESPE AG; ESPE Platz, 82229 Seefeld (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AI, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, GU, HD, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AI, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, GU, HD, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/013924 A1

(54) Title: DENTAL COMPOSITION COMPRISING ETHYLENE IMINE COMPOUNDS AND NON-REACTIVE ACCELERATORS

(57) Abstract: The present invention relates to a composition with enhanced speed of set, especially to a method of making rubber-like elastomers with improved hardening characteristics. In this respect the present invention provides a composition comprising with respect to the cured composition a ethylene imine group containing component A, a SO₂-NH group containing component B and an initiator C. Optionally additives like modifiers, fillers, dyes, pigments, thixotropic agents, flow improvers, polymeric thickeners, surfactants, odorous substances, diluters and flavourings can be added.

DE 197 53 456 A1 mentions that solvents from 0 to 95 % by weight (related to the cured material) selected from polyetherpolyols, polyesterpolyols, polycarbonate polyols, aromatic hydrocarbons, araliphatic hydrocarbons, one- or multifunctional esters of multibasic acids, esters or amides of sulphonic acids may be used.

- 5 DE 100 18 918 A1 describes formulations of catalyst pastes. The catalyst pastes contain 0 to 95 % by weight of an inert solvent chosen from the group of polyether polyols, polyester polyols, aliphatic esters, oils, fats, waxes, aliphatic hydrocarbons, araliphatic hydrocarbons, one- or multifunctional esters of multibasic acids, esters or amides of sulphonic acids. The formulations comprise water (0,1 to 20 %) which is
10 used to influence the speed of set and other properties of the catalyst paste and the cured rubber.

- It is also described that the addition of water to a system of N-alkyl ethylene imines, solvent and initiators alters the speed of set and the conversion rate (G. D. Jones, D. C. MacWilliams, N. A. Braxtor J. Org. Chem. 1965, 1994-2003). The addition of
15 water to uncured polyether precision impression materials, however, may cause sticky surfaces when the impression is cured in the presence of additional water (or saliva in mouth) and may also negatively influence the precision of the impression when impregnated retraction cords or retraction solutions are used.

- A further possibility to enhance the speed of set of formulations comprising
20 compounds having aziridino groups is the additional use of monofunctional compounds together with multifunctional compounds.

- In this respect the German patent application DE 10235990.3 describes a composition, wherein at least one compound has at least two ethylene imine groups and at least one compound has one ethylene imine group. However, the additional
25 use of compounds having one ethylene imine group requires the increase of initiator. The increase of ethylene imine concentration and initiator results in high costs.

- Impression materials based on polyvinyl siloxanes with short setting times are also known. Examples are SplashTM Half-Time (Discus), AquasilTM Fast Set (Dentsply/Caulk), ImprintTM II Quick Step (3M ESPE AG), Take 1 Fast Set (Kerr),
30 Extrude Extra (Kerr).

Dental Composition Comprising Ethylene Imine Compounds and Non-Reactive Accelerators

The invention relates to a dental composition with enhanced speed of set, especially to a method of making rubber-like elastomers with improved hardening characteristics.

Compared to known ethylene imine group containing polyether materials, herein called slow-setting materials, the materials according to the invention have a shorter time of set. These formulations are called fast-setting materials.

Usually the speed of set of dental formulations is adjusted by varying the amount of reactive components, e.g. varying the amount of the polymerizable compound(s) and varying the amount the initiator(s) accordingly and/or varying the amount of the retarder(s).

Aziridines which are also known as ethylene imine compounds can be converted into highly molecular polyamine compounds by means of catalysts which introduce and thus initiate polymerization.

In this respect US 3,453,242 describes curable elastomers from polyethers and ethylene imine derivatives. The polymers are substantially linear in structure and contain ethylene imine groups especially at the ends of the chain to obtain rubber-like products.

DE 100 58 846 A1, DE 197 53 456 A1, DE 100 18 918 A1 describe formulations containing polyether aziridines which show regular setting behavior.

For instance DE 100 58 846 A1 describes the use of N-alkyl aziridino polyethers containing methyl groups in the side chain to improve the properties of the uncured pastes at low temperatures. It is also described that 1 to 35 % by weight of solvents may be used related to the cured material. The solvents are chosen from the group of polyester polyols, aliphatic esters, oils, fats, aliphatic hydrocarbons, one- or multifunctional esters of multibasic acids, esters or amides of sulphonic acids.

CONFIRMATION COPY

However, up to now there is no fast-setting polyether, especially no ethylene imine containing material available.

Considering the clinical situation, in most cases precision impression materials are used to obtain impressions of crowns, inlays, small implants or small bridges
5 (approx. 80 %). In all these cases the dentist does not need a long total working time. In addition a short oral setting time also would be advantageous. Shortening both working time and oral setting time would save time for the dental professionals. Shortening of the whole rather uncomfortable impression taking would be advantageous to the patient.

10

It is thus an object of the invention to alleviate one or more of the problems mentioned above.

It is also an object of the invention to provide a composition with improved properties.

It is another object of the invention to provide a composition, especially a dental
15 polyether composition with enhanced speed of set without essentially altering the elastomeric properties of the cured material.

It has been found that one or more of the above mentioned objects can be achieved by providing a composition as described in the text below.

In this respect the invention relates to a curable dental composition comprising

- 20
- an ethylene imine group containing component A, especially an N-alkyl aziridine polyether,
 - a SO₂-NH group containing component B, comprising e.g. N-alkyl or N-aryl substituted aryl sulfonic acid amides and/or N-alkyl or N-aryl substituted alkyl sulfonic acid amides and non N-substituted sulfonic acid amides,

25

 - an initiator C able to start the curing process of component A,
 - optionally additives D like modifiers, fillers, dyes, pigments, thixotropic agents, flow improvers, polymeric thickeners, surfactants, odorous substances, diluting agent(s) and flavourings.
-

Surprisingly it has been found that by adding a non-reactive accelerator the speed of set of the composition to be hardened can be accelerated without affecting the elastomeric properties of the vulcanized formulation to a considerable extent.

5 Adding such a SO₂-NH group containing component to a curable ethylene imine group containing component enables one to provide compositions that are accelerated with respect to the speed of set without essentially varying the amount of reactive components. The SO₂-NH group containing component usually does not alter the physical properties of the cured material to a considerable extent.

10 Using N,N-disubstituted sulfonic acid amides as component B, that is components containing only a SO₂-NR₂ group, wherein R is not H and thus not comprising a SO₂-NH group with an N-H valence, is not preferred.

Without wishing to be limited to any particular mechanism, it is believed that without at least one NH moiety in the sulfonic acid amid group, not all of the effects intended to be achieved can be reached.

15 Using the present invention, formulations can be provided fulfilling the requirements according to DIN EN ISO 4823:2000 of Type 0 (kneadable), Type 1 (high viscosity), Type 2 (medium viscosity), and Type 3 (low viscosity).

20 The invention provides means to realize short(er) working times of curable compositions, especially dental impression materials, at room temperature and short oral setting times. A total working time at room temperature (23 °C) of less than 3:00 min according to DIN EN ISO 4823:2000 and an oral setting time of less than 3:30 min can be realized.

25 The total working time at room temperature (23 °C) can be measured according to DIN EN ISO 4823:2000. For instance, for ImpregumTM Garant L DuoSoft and Permadyne Garant L 2:1 (3M ESPE AG), both Type 3 regular setting polyether precision impression materials, a working time of 3 min 40 s ± 15 s and 4 min ± 15 s, respectively, is measured.

The oral setting time is given by the manufacturer in the instructions for use. According to DIN EN ISO 4823:2000 the elastomeric property recovery from

deformation of the vulcanized material have to reach values of $\geq 96,5\%$ within the recommended oral setting time. In addition according to DIN EN ISO 4823:2000 the elastomeric property strain in compression of the vulcanized material has to come up to a value within the range of 0,8 to 20,0 % for Type 0 and Type 1 materials and in
5 the range of 2,0 to 20,0 % for Type 2 and Type 3 materials, respectively within the recommended oral setting time.

For instance, for PermadyneTM Garant L 2:1 and ImpregumTM Garant L DuoSoft (3M ESPE AG), both Type 3 regular setting polyether precision impression materials an oral setting time of 3 min 30 s is advised by the manufacturer.

10 Often dental formulations are provided as two-compartment systems in which the two pastes are stored separately. The base paste contains the polymerizable compound(s) and is stored separately from the catalyst paste which contains the initiator.

With respect to shelf-life it is an advantage that the non-reactive accelerators used
15 according to the invention are compatible with the polymerizable compound(s) and with the initiator(s), as well.

An additional paste containing at least one accelerator might also be provided which can be used in dental offices to enhance the setting time of a given polyether impression material according to the dentists needs.

20 The invention provides therefore a low-cost and low-risk method to provide a quick-setting polyether impression material.

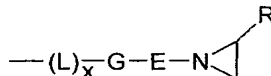
The terms "comprise" and "contain" within the meaning of the invention introduce a non exhaustive list of features. Likewise, the word "one" or "a" is to be understood in
25 the sense of "at least one".

"Working time" according to the invention is the period between complete mixing of the components and the incipient curing of the mixed composition at room temperature. The end of the working time is regarded as the time at which a mixed composition displays pronounced changes such as skin formation or greatly reduced

flowability. At the end of the working time the consistency of the mixed material does not allow the making of a precision impression with the desired detail reproduction and dimensional properties.

- 5 "Oral setting time" according to the invention can be defined as the period between placing the dental tray in the mouth of the patient (the impression material is still processable) and the removal of the dental tray at the time the vulcanized impression material shows the desired elastomeric properties.

- 10 As N-alkyl aziridine polyether (ethylene imine group containing) component A every component can be used which can be vulcanized in the presence of initiator C. The ethylene imine group containing component A comprises at least one ethylene imine group, preferably at least two ethylene imine groups. Those components are known and described e.g. in US 3,453,242, DE 100 58 846 A1, DE 197 53 456 A1, DE 100 18 918 A1 and are generally known as N-alkyl aziridine polyether compositions.
- 15 Suitable components A are N-alkyl substituted aziridines attached to oligomeric and/or polymeric hydrocarbon, ester, ether or siloxane. The attached N-alkyl aziridine can be represented by the formula



wherein

- 20 R represents H, C₁-C₁₂ alkyl, C₂-C₁₂ alkenyl, C₂-C₁₂ alkynyl, C₇-C₁₅ alkylaryl, C₇-C₁₅ arylalkyl, C₃-C₁₂ cycloalkyl, and wherein hydrogen atoms may be replaced by Cl or F and/or wherein up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,
- E represents a C₁ - C₁₈ branched or unbranched hydrocarbon chain wherein up to
25 five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

G represents a group selected from C(O)O, C(O)NR, C(O), C(O)C(O), C(O)(CH₂)_mC(O) with m = 1 to 10, C(S)NR, CH₂,

L represents O, S, NR with x = 0 or 1.

- 5 Component A can be present in an amount in the range of about 10 to about 90 % by weight with respect to the cured composition.

For an impression material component A can be present in an amount in the range of about 35 to about 90 % by weight, or in an amount in the range of about 40 to about 75 % by weight with respect to the cured composition.

- 10 For a of a duplicating material component A can be present in an amount in the range of about 10 to about 25 % by weight, or in an amount in the range of about 12 to about 20 % by weight with respect to the cured composition.

The molecular weight (M_N) of component A before setting can be in the range of about 600 to about 20.000 g/mol, or in the range of about 1.000 to about 10.0000

- 15 g/mol, determined with GPC. Appropriate methods are known by the expert. In addition the determination of the molecular weight is possible using nuclear magnetic resonance spectroscopy (end-group determination). There are also applicable methods described in the literature for organic polyols that may be used like determination of hydroxyl number according to Houben-Weyl, "Methoden der organischen Chemie", 14/2, page 17, Georg Thieme Verlag, Stuttgart, 1963 or
- 20 according to ASTM D2849 Method C.

A very useful method for determination of the molecular weight organic polyols is a GPC method using a combination of PSS SDV 10.000 Å + PSS SDV 500 Å with column dimensions 8x300 mm and a particle size of 5 µm. In addition a pre-column

- 25 PSS SDV 100 Å with column dimensions 8x50 mm and a particle size of 10 µm is used. The eluent is THF stabilized with Jonol running with a flow rate of 1,0 ml/min. The detector is a refractive index detector (RI), the injection volume 100 µl. The samples have a concentration of 1 % (solvent THF). Polystyrol standards are used as the reference.
-

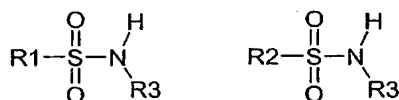
As SO₂-NH group containing component B every component can be used, which is able to accelerate the speed of set of component A.

- A sufficient acceleration of setting (measured at room temperature) of an impression material can be achieved, if e.g. 4,0 % by weight of a non-reactive diluter of a given formulation is replaced by the same amount of component B with the result that the Shore Hardness A (mean value determined from at least three samples) measured after 6 min according to DIN EN ISO 53505 increases by more than about 30 %, or by more than about 40 %, or by more than about 50 % with respect to the value measured for the formulation without component B. Alternatively, e.g. 4,0 % by weight of component B may be added to a given formulation to attain the desired acceleration of set. For very soft rubbers like duplicating materials the acceleration in setting may be measured using a common oscillating rheometer monitoring G' and G''.

- SO₂-NH group containing component B comprises at least one SO₂-NH group, if needed at least two SO₂-NH groups. The SO₂-NH group containing component B can be a molecular or polymeric compound.

- Suitable components B are N-substituted aryl sulfonic acid amides or N-substituted alkyl sulfonic acid amides and non N-substituted alkyl or aryl sulfonic acid amides, that is sulfonic acid amides comprising a SO₂-NH₂ group. In the sulfonamides one hydrogen atom attached to the nitrogen atom of the sulfonamide group can be replaced by an alkyl or aryl radical.

Component B can be represented e.g. by one of the following formulas:



- wherein

R1 represents C₁-C₂₂ alkyl, C₂-C₂₂ alkenyl, C₂-C₂₂ alkynyl, C₇-C₂₂ arylalkyl or C₃-C₂₂ cycloalkyl, and wherein one or more hydrogen atoms may be replaced by Cl or F

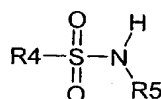
and/or up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

R2 represents C₆-C₁₈ aryl, C₇-C₂₂ alkylaryl, C₂-C₂₂ cycloalkylaryl, C₇-C₂₂ alkenylaryl or C₇-C₂₂ alkynylaryl, wherein one or more hydrogen atoms may be replaced by Cl or

- 5 F and/or up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

R3 represents R1 or R2.

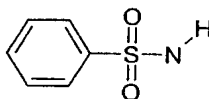
Also polymeric substances comprising the following structure may be used:



- 10 wherein R4 is R1 or R2,

and wherein R5 represents the chemical linkage to the polymer.

Component B contains preferably a sulfonic acid amide or mixture of sulfonic acid amides comprising an aromatic moiety, more preferably a structural element as described in the formula below



15

wherein the aromatic ring may be substituted by one or more substituents.

The sulfonic acid amide can be used alone or in admixture with other different sulfonic acid amides.

- 20 Particularly preferred are benzene sulfonic acid N-butyl amide, p-toluene sulfonic acid N-ethyl amide or a mixture of o-/p-toluene sulfonic acid N-ethyl amide.

Component B can be present in an amount in the range of about 0,01 to about 20,0, or in the range of about 0,1 to about 10,0, or in the range of about 0,2 to about 6,0 % by weight with respect to the cured composition.

The molecular weight of component B can be in the range of about 90 to about 2000 gmol^{-1} or in the range of about 90 to about 300 gmol^{-1} .

As initiator C every component can be used, which is able to start the curing process
5 of component A.

The molar ratio between the initiator and the N-alkyl substituted aziridines of the formulation usually is in the range of gmol^{-1} from about 1,0:0,1 to about 1,0:20,0, or in the range of about 1,0:0,5 to about 1,0:10,0, or in the range from about 1,0:0,8 to about 1,0:3,0.

10 Suitable initiators can be found in O.C. Dermer, G. E. Ham "Ethylenimine and other Aziridines " Academic Press (1969).

Particularly useful are the substituted alkyl sulfonium salts described in US 4,167,618 incorporated herein by reference.

Optionally additives like modifiers, fillers, dyes, pigments, thixotropic agents, flow
15 improvers, polymeric thickeners, surfactants, odorous substances, diluters and flavourings can be added. Additional substances might be useful to further adjust the rheological characteristics.

The additive(s) can be present in an amount in the range of about 10 to about 90 % by weight with respect to the cured composition. For impression materials the
20 additive(s) can be present in an amount in the range of about 10 to about 65 %, or in the range of about 25 to about 60 % with respect to the cured composition. For duplicating materials the additive(s) can be present in the range of about 10 to about 90 %, or in the range of about 20 to about 85 % by weight with respect to the cured composition.

25 Suitable filler(s) are e.g. aluminosilicates, silicic acids, quartz powder, wollastonite, mica powder and diatomaceous earth.

Suitable thixotropic agent(s) are e.g. surface treated silica and/or waxes according to the definition in Ullmanns Enzyklopädie der technischen Chemie, 4. Auflage, Verlag

Chemie, Weinheim, Band 24, page 3. Especially useful are triglycerides as described in DE 197 11 514 A1.

5 Suitable surfactant(s) are polyethers and polyether type materials with special structures such as PluronicTM, SynperonicTM, SilwetTM type materials. Especially useful are substances described in DE 43 06 997 A1.

10 Suitable diluting agent(s) are liquids such as C₁₂-C₁₅ alkyl acetates, liquid derivatives of citric acid, esters of phthalic acid with branched alcohols like bis(2-ethylhexyl)phthalate or polymeric phthalates, C₂-C₁₈ bis(alkyl)esters of C₂-C₆ dicarboxylic acids like dioctylmaleate, aromatic and aliphatic esters of sulfonic acids like MesamollTM, derivatives of di- and tri-ethylen and -propylene glycol, typical aromatic diluters like poly phenyls, dibenzyl toluene, xylyl toluene, dixylyl toluene and polymeric compounds like polyethers, polyesters, polycarbonates, polyolefines. From the group of polymeric compounds, compounds with hydroxyl, ether, alkyl, ester functions are preferred.

15

The shore hardness A of the compositions of the invention is measured according to DIN 53505. To monitor the speed of set time-dependent measurements were performed.

20 The shore hardness A measured after 24 hours usually is in the range from about 40 to about 80 for impression materials and in the range from about 10 to about 40 for duplicating materials.

The elongation at break according to DIN 50125 of the cured impression material of the invention measured 24 hours after mixing the components usually is \geq about 40 %, or \geq about 50 % or \geq about 60 %.

25 The tensile strength according to DIN 50125 of the cured impression material of the invention measured 24 hours after mixing the components usually is \geq about 0,50 MPa, or \geq about 0,55 MPa or \geq about 0,60 MPa.

The elongation at break according to DIN 50125 of the cured duplicating material of the invention measured 24 hours after mixing the components usually is \geq about 80 %, or \geq about 100 % or \geq about 120 %.

5 The tensile strength according to DIN 50125 of the cured duplicating material of the invention measured 24 hours after mixing the components usually is \geq about 0,20 MPa, or \geq about 0,25 MPa or \geq about 0,30 MPa.

As mentioned above dental formulations are often provided as two-component systems.

10 Therefore, the invention also relates to a kit of parts, wherein the base part comprises component A, the catalyst part comprises component C, and wherein component B is present either in the base part or the catalyst part or in the base part and the catalyst part.

15 However, the accelerating effect of component B can also be used to enhance the speed of set of component A containing compositions described in the state of the art.

Presently, the following components are available on the market: Materials of Type 1, (comparable to Permadyne™ Penta™ H, Permadyne™ fest, Impregum™ Penta™ H DuoSoft™), Type 2 (comparable to Impregum™ F, Impregum™ Penta™, Impregum™
20 Penta™ Soft) and Type 3 (comparable to Permadyne™ Penta™ L, Permadyne™ Garant™ 2 : 1, Permadyne™ dünn, Impregum™ Penta™ L DuoSoft™, Impregum™ Garant™ L DuoSoft™). All materials are available from 3M ESPE AG.

25 Therefore, the invention relates also to a kit of parts, wherein component B is comprised in a further part and neither comprised in the catalyst part nor in the base part.

The invention also relates to a method of producing a curable composition comprising the steps a) providing components A, B and C, b) mixing the components.

The dosing of the components can be carried out by sight (strand-length comparison), by weight, via pre-dosed pack units and subsequent manual mixing, from double-chambered cartridges with static mixing tubes or by means of volume dosing systems with downstream static or dynamic mixers.

- 5 A mixing device can be used as it is described in EP 0 492 413 B1 and available on the market as Pentamix™ or Pentamix™ 2. Mixing, however, can also be achieved manually.

A further subject of the invention are packages containing components of the composition, in particular cartridges, bags, prefilled dental trays.

- 10 The composition according to the invention can advantageously be used for modeling of objects or body parts. The composition of the invention is particularly useful as in the dental field, e.g. as impression material, especially as a precision impression material, as a bite registration material or duplicating material.

The composition of the invention does not necessarily comprise water.

- 15 In addition the composition does not necessarily comprise sulfonamides used as active agents in drugs or herbicides.

The invention is hereinafter described by examples. The examples are not intended to limit the scope of the invention.

20

Measurements

- Measuring Shore Hardness A is a very convenient method to obtain data about the degree of vulcanization. The value of Shore Hardness is a common number in dentistry to characterize the vulcanized impression. Time dependant measurements were done according to DIN 53505. For determination of the values three independent measurements were performed. A "Handhärteprüfgerät Zwick 3150" (Zwick GmbH & Co, Ulm) was used as the measuring device. The accuracy of the given values is ± 1 .
- 25
-

Tensile strength and elongation at break were measured according to DIN 50125 Form B. The sample was 6.0 ± 0.1 mm in diameter and 50.0 ± 0.1 mm in lengths (Zugprobe B 6 x 50 DIN 50125). For determination of the values five independent measurements were performed. A "Universalprüfmaschine Zwick 1435" (Zwick
5 GmbH & Co, Ulm) was used as the measuring device.

Formulations:

10 Base Paste 1

- 81,0 % difunctional aziridino polyether (EO (ethylene oxide) / THF (tetra hydro furan) polyether back bone; Mn: 6000)
- 7,0 % fat (triscyclic ester of glycerine)
- 1,0 % surfactant (copolymer EO/PO)
- 15 9,5 % dibenzyl toluene
- 1,5 % diatomaceous earth

Base Paste 2

- 81,0 % difunctional aziridino polyether (Mn: 6000)
- 20 7,0 % fat (triscyclic ester of glycerine)
- 1,0 % surfactant (copolymer of EO/PO)
- 8,8 % dibenzyl toluene
- 1,5 % diatomaceous earth
- 0,7 % imidazole compound

25

Catalyst Paste 1

- 14,0 % sulfonium salt tetrafluoroborate
 - 20,0 % acetyl tributyl citrate
 - 29,0 % unreactive polyether (Mn: 6000)
 - 30 12,0 % dibenzyl toluene
 - 3,0 % surfactant (copolymer EO/PO)
 - 11,0 % diatomaceous earth
-

11,0 % highly dispersed silica, surface treated

Catalyst Paste 2

- 13,5 % sulfonium salt tetrafluoroborate
- 5 19,0 % acetyl tributyl citrate
- 29,0 % unreactive polyether (Mn: 6000)
- 6,5 % dibenzyl toluene
- 3,0 % surfactant (copolymer EO/PO)
- 24,0 % diatomaceous earth
- 10 5,0 % highly dispersed silica, surface treated

I. Varying the amount of sulfonamide

A)

- 15 2,0 g of Base Paste 1 was mixed together with 1,2 g of Catalyst Paste 2, Entry 1. Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of benzene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 2-5.

Table 1

Entry	Amount of benzene sulfonic acid N-butyl amide in		Shore-Hardness A after					
	Elastomer	Base Paste	6 min	8 min	10 min	15 min	30 min	24 h
1	0,00 %	0,00 %	27	37	42	49	52	53
2	1,25 %	2,00 %	38	45	48	51	53	53
3	2,50 %	4,00 %	41	47	50	53	54	54
4	3,75 %	6,00 %	46	49	51	53	54	54
5	5,00 %	8,00 %	47	50	51	53	54	54

Table 2

Entry	Amount of benzene sulfonic acid N-butyl amide			
	Elastomer	Base Paste	Tensile Strength	Elongation at break
1	0,00 %	0,00 %	1,04 ± 0,03 MPa	78 ± 6 %
3	2,50 %	4,00 %	0,99 ± 0,05 MPa	75 ± 8 %
5	5,00 %	8,00 %	1,12 ± 0,15 MPa	91 ± 23 %

B)

- 5 The 2,0 g of altered Base Paste 1 that already contains 8,00 % of benzene sulfonic acid N-butyl amide (CAS-No 3622-84-2) was used together with 1,2 g of Catalyst Paste 2, Entry 5.

Acetyl tributyl citrate (CAS-No 77-90-7) in the Catalyst Paste 2 was replaced by the same amount of benzene sulfonic acid N-butyl amide (CAS-No 3622-84-2). 2,0 g of the base paste according to Entry 5 was used with 1,2 g of the altered catalyst pastes, Entry 6 - 7.

Table 3

Entry	Amount of benzene sulfonic acid N-butyl amide in			Shore-Hardness A after					
	Elastomer	Base Paste	Catalyst Paste	6 min	8 min	10 min	15 min	30 min	24 h
5	5,00 %	8,00 %	0,00 %	47	50	51	53	54	54
6	6,25 %	8,00 %	3,33 %	47	50	52	53	53	53
7	7,50 %	8,00 %	6,67 %	48	51	53	53	53	53

The addition of component B does not necessarily have a significant effect on the elastomeric properties of the cured composition. Tensile strength and elongation at break remain essentially unchanged.

- 5 As can be inferred especially from Table 1 a sufficient Shore Hardness A can be achieved after a shorter period of time, if component B is present in the composition.

The desired effect can be already achieved at a considerable low concentration of the sulfonamide component. Further increasing the concentration does not necessarily enhance the speed of set.

10 II. Comparison: Sulfonamide used in the catalyst paste vs. sulfonamide used in the base paste

Base Paste 2 and Catalyst Paste 1 were altered. 2,0 g of the used base paste was mixed together with 1,1 g catalyst.

- 15 Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of bezene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 8.

Acetyl tributyl citrate (CAS-No 77-90-7) in the catalyst paste was replaced by the same amount of bezene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 9.

Table 4

20

Entry	Amount of benzene sulfonic acid N-butyl amide in			Shore-Hardness A after					
	Elastomer	Base Paste	Catalyst Paste	6 min	8 min	10 min	15 min	30 min	24 h
8	2,26 %	3,50 %	0,00 %	28	36	40	45	46	47
9	2,26 %	0,00 %	6,40 %	29	36	40	43	48	49

Usually there is no significant difference whether the sulfonamide is used in the base paste or in the catalyst paste.

III. Comparison: Use of mixture of o-/p- toluene sulfonic acid N-ethyl amide vs. use of benzene sulfonic acid N-butyl amide and p- toluene sulfonic acid N-ethyl amide

2,0 g Base Paste 2. was mixed together with 1,2 g of Catalyst Paste 2, Entry 10.

5

Base Paste 2 was altered. 2,0 g of altered Base Paste 2 was mixed together with 1,2 g of Catalyst Paste 2.

Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of mixture approx. 70 : 30 mixture of o-/p- toluene sulfonic acid N-ethyl amide (CAS-No 8047-99-2, 26914-52-3), Entry 11.

10

Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of benzene sulfonic acid N-butyl amide (CAS-No 80-39-7), Entry 12.

Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of benzene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 13.

15

Table 5

Entry	Used sulphonamide	Amount of Sulfonamide in		Shore-Hardness A after					
		Elastomer	Base Paste	6 min	8 min	10 min	15 min	30 min	24 h
10	None	0,00 %	0,00 %	16	28	34	42	48	50
11	o-/p-toluene sulfonic acid N-ethyl amide	3,75 %	6,00 %	31	38	41	46	49	50
12	p-toluene sulfonic acid N-ethyl amide	3,75 %	6,00 %	34	40	42	47	50	51
13	benzene sulfonic acid N-butyl amide	3,75 %	6,00 %	30	37	42	46	50	50

IV. Comparison: Use of bezene sulfonic acid N-butyl amide vs. benzene sulfonic acide amide

Base Paste 2 was altered. 2,0 g of altered Base Paste 2 was mixed together with 1,2 g of Catalyst Paste 2.

- 5 Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of bezene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 13.

Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of benzene sulfonic acid amide (CAS-No 98-10-2), Entry 14.

10 Table 6

Entry	Used sulphonamide	Amount of Sulfonamide in		Shore-Hardness A after					
		Elasto-mer	Base Paste	6 min	8 min	10 min	15 min	30 min	24 h
13	benzene sulfonic acid N-butyl amide	3,75 %	6,00 %	30	37	42	46	50	50
14	benzene sulfonic acid amide	3,75 %	6,00 %	33	40	42	47	49	49

V. Comparison: use of benzene sulfonic acid N-butyl amide vs. benzene sulfonic acid N-butyl N-methyl amide

15

Base Paste 2 was altered. 2,0 g of altered Base Paste 2 was mixed together with 1,2 g of Catalyst Paste 2.

Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of bezene sulfonic acid N-butyl amide (CAS-No 3622-84-2), Entry 13.

Di-benzyl toluene (CAS-No 26898-17-9) in the base paste was replaced by the same amount of benzene sulfonic acid N-butyl N-methyl amide (CAS-No 119059-69-7), Entry 15.

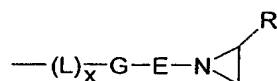
5 Table 6

Entry	Sulphonamide	Amount of Sulfonamide in		Shore-Hardness A after					
		Elasto-mer	Base Paste	6 min	8 min	10 min	15 min	30 min	24 h
13	benzene sulfonic acid N-butyl amide	3,75 %	6,00 %	30	37	42	46	50	50
15	benzene sulfonic acid N-butyl N-methyl amide	3,75 %	6,00 %	23	33	37	43	48	49

Claims:

1. Dental composition comprising with respect to the cured composition
- 5 N-alkyl aziridine polyether as component A,
 SO₂-NH group containing component B
 initiator C,
 optionally additives D comprising modifiers, fillers, dyes, pigments, thixotropic
 agents, flow improvers, polymeric thickeners, surfactants, odorous
 10 substances, diluting agent(s) and flavourings.

2. The composition according to claim 1, wherein component A comprises a
 structure element represented by the following formula



- 15 wherein

R represents H, C₁-C₁₂ alkyl, C₂-C₁₂ alkenyl, C₂-C₁₂ alkynyl, C₇-C₁₅ alkylaryl,
 C₇-C₁₅ arylalkyl, C₃-C₁₂ cycloalkyl, and wherein hydrogen atoms may be
 replaced by Cl or F and/or wherein up to five carbon atoms may be replaced
 by atoms or group of atoms selected from O, CO, N, S,

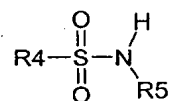
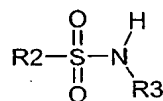
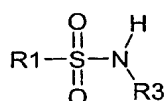
- 20 E represents a C₁ - C₁₈ branched or unbranched hydrocarbon chain wherein
 up to five carbon atoms may be replaced by atoms or group of atoms selected
 from O, CO, N, S,

G represents a group selected from C(O)O, C(O)NR, C(O), C(O)C(O),
 C(O)(CH₂)_mC(O) with m = 1 to 10, C(S)NR, CH₂,

- 25 L represents O, S, NR with x = 0 or 1.

3. The composition according to anyone of the preceding claims comprising
 component B in an amount of about 0,01 % by weight to about 20,00 % by
 weight.

4. The composition according to anyone of the preceding claims wherein component B comprises aryl sulfonic acid amides and/or alkyl sulfonic acid amides.
- 5
5. The composition according to anyone of the preceding claims wherein component B comprises N-alkyl or N-aryl substituted aryl sulfonic acid amides and/or N-alkyl or N-aryl substituted alkyl sulfonic acid amides.
- 10 6. The composition according to anyone of the preceding claims, wherein component B is represented by at least one of the following formulas:



15 wherein

R1 represents C₁-C₂₂ alkyl, C₂-C₂₂ alkenyl, C₂-C₂₂ alkynyl, C₇-C₂₂ arylalkyl or C₃-C₂₂ cycloalkyl, and wherein one or more hydrogen atoms may be replaced by Cl or F and/or up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

20 R2 represents C₆-C₁₈ aryl, C₇-C₂₂ alkylaryl, C₂-C₂₂ cycloalkylaryl, C₇-C₂₂ alkenylaryl or C₇-C₂₂ alkynylaryl, wherein one or more hydrogen atoms may be replaced by Cl or F and/or up to five carbon atoms may be replaced by atoms or group of atoms selected from O, CO, N, S,

R3 represents H, R1 or R2.

25 R4 is R1 or R2,

and R5 represents the chemical linkage to a polymer.

7. The composition according to anyone of the preceding claims, wherein the molecular weight of component B is in the range of 90 to 2000 g/mol¹.
 8. The composition according to anyone of the preceding claims, wherein
5 component B comprises benzene sulfonic acid N-butyl amide or p-toluene sulfonic acid N-ethyl amide, o-toluene sulfonic acid N-ethyl amide, benzene sulfonic acid amide or a mixture of o-/p- toluene sulfonic acid N-ethyl amide.
 9. The composition according to anyone of the preceding claims, wherein initiator C
10 is selected from the group of protonating or alkylating agents or wherein the initiator C generates protons and/or reactive alkylating agents in a chemical reaction.
 10. The composition according to anyone of the preceding claims having a working
15 time at 23 °C of equal or less than 3:30 min according to DIN EN ISO 4823:2000 and/or an oral setting time of equal or less than 3:30 min
 11. Kit of parts, comprising a base and a catalyst part, wherein the base part
20 comprises component A, the catalyst part comprises component C, and wherein component B is present either in the base part or the catalyst part or in the base part and the catalyst part, wherein components A, B and C have the meaning as defined in the preceding claims.
 12. Kit of parts, wherein the base part comprises component A, the catalyst part
25 comprises component C, and wherein component B is comprised in a further part and neither comprised in the catalyst part nor in the base part, wherein components A, B and C have the meaning as defined in the preceding claims.
 13. Method of producing a dental composition according to one of the claims 1 to 10
30 comprising the steps a) providing components A, B and C, b) mixing the components.
-

14. Use of a component B containing composition for enhancing the speed of set of a component A and C containing dental composition, wherein components A, B and C have the meaning as defined in the preceding claims.

5

15. Use of the composition according to anyone of claims 1 to 9 or the kit of parts according to claim 10 or 11 for modeling of objects or body parts, preferably as dental impression, bite registration or dental duplicating material.

10

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP2004/007928

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A61K6/10		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 A61K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 600 766 A (MASUDA ISAO ET AL) 15 July 1986 (1986-07-15) column 1, lines 26-40 column 2, lines 29-43 claims; examples 2, 18, 19	1
A	DE 197 53 456 A (ESPE DENTAL AG) 10 June 1999 (1999-06-10) cited in the application page 2, lines 3-48 claims	1-15
A	DE 100 18 918 A (3M ESPE AG) 15 November 2001 (2001-11-15) cited in the application claims	1-15
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *Z* document member of the same patent family		
Date of the actual completion of the international search 6 December 2004		Date of mailing of the international search report 15/12/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Böhm, I

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/007928

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 130 348 A (ELLRICH KLAUS ET AL) 14 July 1992 (1992-07-14) column 1, lines 8,9 column 2, lines 33-57 claims	1
A	DE 100 26 852 A (3M ESPE AG) 13 December 2001 (2001-12-13) page 2, paragraph 2 page 3 claims	1-3, 11-15
A	WO 01/52792 A (WANKE ERICH ; ROAS PETER (DE); 3M ESPE AG (DE); ECKHARDT GUNTHER (D) 26 July 2001 (2001-07-26) claims	1
A	US 3 453 242 A (JOCHUM PETER ET AL) 1 July 1969 (1969-07-01) cited in the application column 2, lines 32-37 column 3; figure 1	1,2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP2004/007928

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4600766	A	15-07-1986	JP 1688722 C	11-08-1992
			JP 3056580 B	28-08-1991
			JP 60090219 A	21-05-1985
			CA 1226988 A1	15-09-1987
			EP 0141345 A2	15-05-1985
			KR 9210149 B1	16-11-1992
DE 19753456	A	10-06-1999	DE 19753456 A1	10-06-1999
DE 10018918	A	15-11-2001	DE 10018918 A1	15-11-2001
			AU 4654201 A	30-10-2001
			WO 0179328 A1	25-10-2001
			EP 1274769 A1	15-01-2003
			JP 2003533556 T	11-11-2003
			US 2003153726 A1	14-08-2003
US 5130348	A	14-07-1992	DE 3932989 A1	11-04-1991
			AT 109962 T	15-09-1994
			AU 643459 B2	18-11-1993
			AU 6374390 A	11-04-1991
			CA 2026734 A1	04-04-1991
			DE 59006828 D1	22-09-1994
			EP 0421371 A2	10-04-1991
			ES 2057306 T3	16-10-1994
			JP 2967236 B2	25-10-1999
			JP 3120205 A	22-05-1991
DE 10026852	A	13-12-2001	DE 10026852 A1	13-12-2001
			AU 6232301 A	11-12-2001
			WO 0192374 A1	06-12-2001
			EP 1290063 A1	12-03-2003
			US 2004014907 A1	22-01-2004
WO 0152792	A	26-07-2001	DE 10001747 A1	26-07-2001
			AU 772056 B2	08-04-2004
			AU 2516001 A	31-07-2001
			WO 0152792 A1	26-07-2001
			EP 1248588 A1	16-10-2002
			JP 2003520216 T	02-07-2003
			US 2003109596 A1	12-06-2003
US 3453242	A	01-07-1969	DE 1544837 A1	09-04-1970
			DE 1745810 A1	02-01-1970
			FR 1423660 A	07-01-1966
			GB 1044753 A	05-10-1966

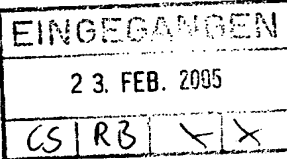
PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

3M ESPE AG
ESPE Platz
82229 Seefeld
ALLEMAGNE



NOTIFICATION OF RECEIPT OF DEMAND BY COMPETENT INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))

Date of mailing (day/month/year) 17-02-2005

Applicant's or agent's file reference

58741W0003 PE-SA1 PCT

IMPORTANT NOTIFICATION

International application No.

PCT/EP2004/007928

International filing date (day/month/year)

16/07/2004

Priority date (day/month/year)

17/07/2003

Applicant

3M ESPE AG

1. The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

04/02/2005

2. This date of receipt is:

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ **ATTENTION:** That date of receipt is **after** the expiration of 19 months from the priority date. Consequently, in respect of some Offices, the demand does not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)) and the acts for entry into the national phase must therefore be performed within 20 months from the priority date (or later in some Offices). **However**, in respect of some other Offices, the time limit of 30 months (or later) may nevertheless apply. See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

- ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Netherlands
Tel.: (+ 31-70) 340-2040
Fax: (+ 31-70) 340-3016

Authorized officer

CARDENAS C E

Tel. (+ 31-70) 340-3370

Form PCT/IPEA/402 (April 2002; reprint January 2004)

(14/02/2005)

